5120 – Advanced Metallics Branch – Highlights – FY99

Branch members were integral team members with GE and P&W, plus provided technical management in both the HSR/EPM and AST disk and airfoil programs. These efforts lead to:

a) The successful development of a new powder metallurgy disk alloy, which is slated to be the first significant new disk alloy introduced by GE and P&W in 15 years. (Gabb, Gayda, Garg, Ellis, Telesman, Kantzos)

b) Full production specifications were defined for a next generation single crystal turbine airfoil alloy that has 50°F higher temperature capability than today's production alloys. Processing steps to reduce the interaction between the airfoil alloy substrate and bond coat were also proposed, tested, and recommended. (MacKay, Ritzert, Garg)

Provided answers to key questions regarding the feasibility of IN-718 sheet intended for the heater head of a Stirling engine as a power source on deep space satellite missions to Pluto. The issues of Cr loss in the vacuum of space and creep strength for the 100,000 hour design life were addressed both analytically and experimentally. A new heat treatment was also recommended and adopted. (Bowman)

A program for maturing Cu-8Cr-4Nb for use in Reusable Launch Vehicles established that alloy production is both reproducible and scalable to commercial quantities. In addition, the results confirmed the physical and mechanical property advantages over NARloy-Z, which can lead to at least a 10X life improvement. (Ellis, Yun, Lerch)

A new in-situ toughened $MoSi_2$ base alloy was developed, with a toughness of 15 $MPa\sqrt{m}$ and thermal conductivity twice as high as the best available monolithic ceramic, AS-800. (Hebsur)

Developed two new NiAl-based bond coat versions, with either ternary element or AlN particulate additions, that produced exceptional thermal barrier coating lives. (Noebe, Bowman, Hebsur, Miller)

Showed that a new lower cost method for producing TiAl sheet produced a good balance of strength, ductility, creep, and fatigue properties, thus enabling its consideration for HSCT and RLV applications. (Draper, Bowman, Gayda, Whittenberger, Locci, Bartolotta)

Directional Solidification of NiAl-based Alloys for Improved Elevated Temperature Strength and Room Temperature Toughness

J. D. Whittenberger, S. V. Raj, I. E. Locci, and J. A. Salem

Efforts are underway to replace superalloys used in the hot sections of gas turbine engines with materials possessing better mechanical and physical properties. Alloys based on the intermetallic NiAl have demonstrated potential; however they generally suffer from low fracture resistance (toughness) at room temperature and poor strength at elevated temperature. Directional solidification of NiAl alloyed with both Cr and Mo has yielded materials with useful toughness and strength values.

The intermetallic alloy NiAl has been proposed as an advanced material to extend the maximum operational temperature of gas turbine engines by several hundred degrees centigrade. Additionally this intermetallic displays a lower density (~30 % less) and a higher thermal conductivity (4 to 8 times) than conventional superalloys as well good high temperature oxidation resistance. Unfortunately, unalloyed NiAl has poor elevated temperature strength (~50 MPa at 1027 ºC) and low room temperature fracture toughness (about 5 MPa•√ m).

Directionally-solidified NiAl eutectic alloys are known to possess a combination of high elevated temperature strength and good room temperature fracture toughness. Research [refs. 1 & 2] demonstrated that a NiAl matrix containing a uniform distribution of very thin Cr plates alloyed with Mo possessed both increased fracture toughness and elevated temperature creep strength. While attractive properties were obtained, these studies were conducted at low growth rates (≤ 19 mm/h) which are considered to be economically unviable. Hence an investigation of the strength/toughness behavior of directionally solidified NiAl-(Cr,Mo) after growth at faster rates was warranted. If the mechanical properties do not deteriorate with increased growth rates, directional solidification could offer an economical commercial production means to introduce NiAl-based alloys into gas turbine engines.

An investigation at Glenn Research Center at Lewis Field was undertaken to study the effect of directional solidification growth rate on the microstructure, room temperature fracture toughness and 1027 ºC strength of a Ni-33Al-31Cr-3Mo eutectic alloy. The directionally solidified rates varied between 7.6 and 508 mm/h [ref. 3]. Essentially fault-free alternating (Cr,Mo)/NiAl lamellar plates microstructures were formed during growth at and below 12.7 mm/h, while cellular microstructures with the (Cr,Mo) phase in a radial spoke-like pattern were developed at faster growth rates. The compressive strength at 1027 ºC continuously increased with increasing growth rate and did not indicate a maxima as was reported for directionally solidified Ni-33Al-34Cr. Surprisingly samples with the lamellar plate microstructure possessed a room temperature fracture toughness of ~12 MPa•√ m, while all the alloys with a cellular microstructure had toughnesses of about 17 MPa•√ m. These results are significant since they clearly demonstrate that Ni-33Al-31Cr-3Mo can be directionally solidified at much fast growth rates without any observable deterioration in its mechanical properties. Thus the potential to produce strong, tough NiAl-based eutectics at commercially acceptable growth rates exists. Additionally testing and alloy optimization studies to are currently underway.

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Creep Properties of NiAl-1Hf Single Crystals

J. D. Whittenberger, I. E. Locci, R. Darolia, R. Bowman

NiAl-1Hf single crystals have been shown to be quite strong at 1027 ºC with strength levels approaching those of advanced Ni-base superalloys; however initial testing has indicated that the properties might not be reproducible. Study of the 1027 ºC creep behavior of four different NiAl-1Hf single crystal ingots subjected to several different heat treatments has indicated that strength lies in a narrow band; thus it is concluded that the mechanical properties are reproducible.

Recent investigations [ref. 1] of the intermetallic NiAl have confirmed that minor alloying additions combined with single crystal growth technology can produce elevated temperature strength levels approaching those of Ni-base superalloys. For example General Electric alloy AFN-12 {Ni-48.5 (at. %)Al-0.5Hf-1Ti-0.05Ga} has a creep rupture strength equivalent to Rene' 80 combined with a ~30 % lower density, four times better thermal conductivity and the ability to form a self protective alumina scale in aggressive environments.

Although the compositions of strong NiAl single crystals are relatively simple, the microstructures are complex and are dependent on the heat treatment and small ingot to ingot variations in alloy chemistry [ref. 2]. Additionally, initial testing [ref. 3] suggested a strong dependence between microstructure and creep strength. If these observations were true, the ability to utilize NiAl single crystal rotating components in turbine machinery could be severely limited.

In order to develop an understanding of the possible limitations in the creep response of high strength NiAl single crystals, an in-depth investigation [ref. 4] of the effect of heat treatment on the microstructure and subsequent 1027 ºC creep behavior of [001]-oriented NiAl-1Hf with a nominal chemistry of Ni-47.5Al-1Hf-0.5Si was initiated at the Glenn Research Center at Lewis Field. This alloy was selected since four ingots, grown over a number of years and possessing slightly different compositions, were available for study. Specimens taken from the ingots were subjected to several heat treatment schedules, examined by transmission electron microscopy and tested in both compression and tension.

An example of the microstructure found in a [001]-oriented NiAl-1Hf specimen after a solution treatment at 1317 ºC for 50 hours followed by air cooling shows the NiAl matrix contains a uniform distribution of nanometer scale G-phase ($Ni_{16}Hf_6Si_7$) precipitates. Other heat treating schedules produced microstructures with nanometer sized G-phase cubes and plates or, in an extreme case, all the G-phase was converted to Heusler (Ni_2AlHf) particles.

The results of 1027 ºC creep strength - strain rate testing indicates that with one exception, all the strength values lie in a narrow band that spans six orders of magnitude in strain rate. The only factor which produced results outside this band was the heat treatment schedule that dissolved all the G-phase and replaced it with Heusler precipitates.

These results lead to the important practical conclusion that the elevated temperature creep properties of NiAl-1Hf single crystals are reproducible and are not affected by small variations in alloy chemistry which exist from ingot to ingot or different initial distributions of G-Phase in the heat treated alloy. The only variable in this study that produced a significant and deleterious effect on mechanical strength was a post solution heat treatment which lead to the complete disappearance of G-phase in favor of Heusler precipitates.

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Very Long Term Oxidation of Titanium Aluminides

I. E. Locci and J. L. Smialek

Titanium aluminides (TiAl) are of great interest for intermediate-temperature (600°C-850°C) aerospace and power generation applications because they offer significant weight savings compared to today's nickel alloys. TiAl alloys are being investigated for low-pressure turbine blades applications, exhaust nozzle components and compressor cases in advanced subsonic and supersonic engines [1].

Significant progress has been made in understanding the fundamental aspects of the oxidation behavior of binary TiAl alloys [2-3]. However, most of this work has concentrated on short term (< 1000 hours), high temperature (900°C-1000°C) exposures. Also, little data is available in the literature regarding the oxidation behavior of the quaternary and higher order engineering alloys. This is especially true for the very long-term, low temperature conditions likely to be experienced during aerospace applications.

An investigation at the Glenn Research Center at Lewis Field was undertaken to characterize the long-term oxidation behavior of various model and advanced titanium aluminides for periods up to 7000 hours (h) at 704°C in air using a high-resolution field emission scanning electron microscope. Also a unique surface treatment technique [4] developed to improve the oxidation resistance of TiAl was evaluated. The alloys included in this investigation are listed in Table 1. Typical alloy compositions, the specific weight changes and the scale thickness measured for each alloy after exposure to 700ºC for 7000 h in air are also included in Table 1.

The response to the long-term exposure is reflected on the specimen weight gained for the different alloy compositions. The binary TiAl alloy is the only alloy where the scale was not adherent and tended to spall-off. Cr, which is normally added to the alloy for enhanced mechanical properties, was extremely detrimental to oxidation resistance. The presence of Nb as a ternary or quaternary addition was extremely beneficial, minimizing the weight gained even when Cr was present in the alloy. The TiAl-2Cr-2Nb alloy benefited further from the phosphoric acid surface treatment [4], which significantly reduced the oxidation rate. The more advanced alloys, which contain a higher number of added elements, showed reduced oxidation rates. All the alloys formed complex alloy scales that required detailed microscopy analyses. Microprobe spectrometry and high resolution scanning microscopy were used to reveal the key features observed in the alloy scales. These microstructural differences are being used to explain and predict the oxidation response that advanced TiAl alloys will exhibit in actual service.

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Alloy (at.%)	*Al*	*Ti*	*Cr*	*Nb*	*Mn*	*W*	*Wt. Change/area (mg/cm^2)*	*Scale Thickness (μm)*
TiAl	48.07	51.93	-	-			4.28 (spalled)	20
TiAl-2Cr	47.99	50.01	2.00				10.29	150
TiAl-2Nb	47.99	50.01	-	2.00			1.43	12
TiAl-2Cr-2Nb	48.03	47.97	2.00	2.00			2.04	15
TiAl-2Cr-2Nb + Surface Treated	48.03	47.97	2.00	2.00			0.57	6
XD	47.39	49.24	2.04	1.14	0.21		0.86	9
K5	46.5	48.3	2	3		0.2	1.05	6
Alloy 7	46	48		5		1	0.4	5
WMS	47	50		2	1	0.5	0.61	4

Compositions (in at.%), weight gained and scale thickness for model and engineering TiAl alloys exposed to 700ºC for 7000 hours in air.

1999 HIGHLIGHTS- CERAMICS BRANCH (5130)

1999- ANOTHER YEAR OF CHANGE

- **Complete turnover of R&T Base Program**
  - Hitemp and Fast Quiet Engine come to an end
  - Hot Propulsion Components, Supersonics and Zero CO2 Emissions begin
    - New effort in ZrO2 fuel cells
    - Continued interdisciplinary effort in cooled silicon nitride
    - Continued effort in oxide ceramics
  - Expanded activity in hypersonics

- **Focused Aeronautics**
  - EPM ends, UEET starts
    - Continued CMC effort
    - New effort supporting TBC coatings
    - Arc lamp combustor rig brought to operational status
  - Role in REVCON

- **Space Transportation**
  - Stable funding so far in an unstable program

- **Other activities**
  - Continued active role in Technology Utilization, Strategic Research Fund, and Glennan MEMS initiative

AWARDS

R&D-100 Award- Affordable, Robust Ceramic Joining Technology: M. (Jay) Singh.

Forty-five Year NASA Service Award: Earl R. Hanes, Jr.

1999 NASA Public Service Medal: M. (Jay) Singh

1999 NASA Exceptional Service Medal: Andrew J. Eckel

Group Achievement Award from Marshall Space Flight Center for Simplex Turbopump CMC Blisk: Andrew J. Eckel and James D. Kiser

1999 Best Poster/Paper Award, Engineering Ceramics Division, The American Ceramic Society: M. (Jay) Singh

1999 National Academy of Engineering-Frontiers of Engineering (NAE-FOE) Selection: M. (Jay) Singh

2000 Richard M. Fulrath Award, The American Ceramic Society: M. (Jay) Singh

TECHNICAL ACCOMPLISHMENTS

Aeronautics

Whisker Reinforced Oxide Matrix Composites: Mullite whiskers have been incorporated into oxide composites as a reinforcing phase. In the initial efforts of this study a rigid, machinable whisker preform was fabricated by casting the whisker precursor slurry into the desired final shape and heat treating under controlled conditions. Fabrication of the whisker reinforced composite was completed by coating the whiskers with a sol-gel derived interface coating followed by infiltration with an oxide matrix. In the next stage of whisker composite development, the heat treatment conditions for whisker formation were altered to allow for incorporation of continuous polycrystalline fibers in the composite. The continuous fibers were pulled through a slurry of the whisker precursor material and wound into fiber mats. These mats were stacked, warm-pressed, and then heat-treated. The resulting microstructure was a continuous fiber reinforced oxide composite with a randomly oriented whisker matrix. This type of microstructure allows for directional strengthening from the continuous fiber phase and toughening and resistance to delamination from the interlocking, randomly oriented whisker matrix. **(Martha Jaskowiak and John Setlock)**

BN and Si-Doped BN form Single Source Molecular Precursor. A method was developed for depositing BN at low temperatures using a neat liquid delivery system. Si levels of 10-15 percent have been attained in doped materials. Addition of dopant is expected to increase environmental durability. Thin coatings have been produced on ceramic fibers, while maintaining fiber flexibility and strength. Commercialization potential is under evaluation by GLITECH. The process is of interest both for ceramic matrix composites and in the semiconductor industry. **(Frances Hurwitz)**

CMC Tailcone. GRC, in partnership with Allison, Northrop Grumman and the Air Force, contributed to the development of processing parameters for a Blackglas™ CMC tailcone that has been successfully engine tested on an Allison 2100. The material also is of interest as an exhaust tailcone on the Allison 3007 and for the Global Hawk Tier II aircraft. **(MaryAnn Meador (5160) and Frances Hurwitz)**

Filled Polymers for CMC Matrix. Parameters have been identified which contribute to low viscosity polymer/filler systems for use in CMC fabrication. They have the potential to reduce the number of infiltration/ pyrolysis cycles from 10 to 7. **(Frances Hurwitz).**

Affordable, Robust Ceramic Joining Technology (ARCJoinT) Transferred to Bechtel Bettis, Inc.: Advanced silicon carbide-based ceramics and fiber-reinforced composites are being actively considered for a number of components in the nuclear industry. The ARCJoinT- ceramic joining technology, which was developed in-house, was successfully transferred to Bechtel Bettis, Inc., Bettis Atomic Power Laboratory, West Mifflin, PA under a reimbursable for the fabrication and joining of ceramic components for nuclear applications. **(M. (Jay) Singh and Rich Dacek)**

Dependence Of Crystallographic Texture On Processing Parameters For Directionally Solidified Alumina-YAG Established: Oxide-oxide eutectics are being investigated as a means to produce in-situ composites. The alumina-YAG eutectic combines two highly creep resistant oxides to produce a material with excellent high temperature properties. Critical material properties (CTE, residual stress, and deformation resistance) are dependent on the crystallographic texture. Comprehensive work at Glenn demonstrated that both the axes of growth and the alignment between phases changes as a function of solidification rate, and identified regimes of single crystal and mixed behavior. To our knowledge, this is the first documented incidence of such behavior in ceramic eutectic systems. **(Serene Farmer, Ali Sayir, Tom Sabo)**

International Meeting "New Developments in High Temperature Materials" Organized: Ali Sayir (CWRU) and Serene C. Farmer from NASA GRC, and Prof. Nils Technische from the University of Hamburg, Germany organized the meeting which was held in Europe in August 1998. Sponsors included NASA Glenn, the Air Force Office of Scientific Research, the United States Office of Naval Research (ONR), European Office of Aerospace, Research and Development (EOARD), and the Marmara Research Center. The purpose of the meeting was to bring scientists and engineers in the European and United States communities together in order to gain an international perspective on new developments in the high temperature ceramics field. Forty selected peer reviewed papers were published in a special issue of the Journal of the European Ceramic Society, September 1999, edited by Sayir and Farmer.

Arc Lamp Combustor Durability Rig: A new thermal-mechanical test system for conducting combustor liner durability tests is currently in operation. Lamp and rig checkouts, software development, and the exposure of a thermocoupled silicon carbide / silicon carbide (SiC/SiC) cylinder are being completed in preparation for significant testing to be conducted under the Ultra-Efficient Engine Technology Program (UEET). The unique capabilities of the rig will allow SiC/SiC ceramic matrix composite (CMC) cylinders to be exposed to thermal conditions similar to those encountered by a combustor liner in an aircraft engine. Sub-zero refrigerated air (as low as -50°C) impinging on the outside wall of the cylinder, and arc-lamp induced temperatures at the inside wall in excess of 1500°C will create thermal gradients through the thickness of the CMC. The quick response of the lamp will allow for rapid heat ups and thermal cycling. **(Jon Goldsby and Mike Halbig)**

Constituent Guidelines Developed For Enhancing Strength Retention Of SiC/SiC Composites At Intermediate Temperatures In Oxidizing Environments: Under the EPM program, it has been determined that the keys to obtaining long life for uncracked SiC/SiC melt-infiltrated composites in oxidizing environments at intermediate temperatures are to utilize (1) environmentally resistant interphase coatings (such as Si-doped BN), and (2) constituent types that maximize composite modulus. For cracked composites, the key is to utilize (1) environmentally resistant interphase coatings, and (2) constituent types that maximize ultimate tensile strength. For both cases, it is important to avoid carbon in the interphase coating that may be introduced deliberately or as a result of poor decomposition of the fiber sizing. **(Jim DiCarlo, Greg Morscher, Linus Thomas-Ogbuji (5160), and Hee Mann Yun (5120))**

Factors Controlling Intermediate Temperature Embrittlement of Hi-Nicalon™/BN/MI-SiC Composites Quantified: Three factors control the stress-rupture properties of SiC/BN/SiC composites at intermediate temperatures in air: the durability of the BN interphase, the amount and extent of matrix cracking, and the fiber architecture. BN oxidizes resulting in fiber-to-fiber fusion and fiber embrittlement in exposed matrix cracks. Matrix cracks form upon loading but then also grow during the test as the interphase is removed and replaced with the oxidation products. The woven architecture promotes close fiber-to-fiber contact that hastens the embrittlement process. Also, the woven architecture by it's nature allows for large unbridged matrix crack regions that cause fairly large stress-concentrators on the bridging fibers that bound the unbridged region of a matrix crack. Failure of these highly stressed fibers is the likely "trigger" for composite failure at intermediate temperatures. All of these factors have been incorporated into a probabilistic model for stress-rupture of this system at intermediate temperatures. **(Greg Morscher)**

Modal Acoustic Emission Used to Monitor Damage During Stress-Rupture of SiC/SiC Composites: Modal (wide-band) acoustic emission (AE) was successfully used to monitor and locate the occurrence of matrix cracking during stress-rupture tests of SiC fiber reinforced SiC matrix composites tested at elevated temperatures. Even though sensors are attached to the sample in the water-cooled grips, post-test examination showed that the modal AE technique was capable of locating the source events within one millimeter of where they occurred. The progression of local damage accumulation during a test could be used to predict the ultimate failure location of a composite during a test. **(Greg Morscher, Janet Hurst, Dan Gorican)**

Rapid Prototyping of Ceramics: GRC and Case Western Reserve University researchers have developed a rapid prototyping capability for fabrication of e.g. silicon nitride and aluminum oxide ceramics. Starting with a CAD file of the part to be made, permanent and removable mold components for gel casting of ceramic slips are made by stereolithography and Sanders machines, respectively. The gel cast part is dried and sintered to final shape. Complex parts can be fabricated in a couple off weeks. A silicon nitride rocket nozzle made by this technique performed remarkably well in tests recently completed at GRC. **(Ram Bhatt, Jim Cawley, and Ray Babuder)**

Feasibility Of Cooled Silicon Nitride Airfoil For Turbine Applications Demonstrated: An in-situ toughened silicon nitride generic airfoil with internal cooling passages fabricated by rapid prototyping technology were successfully burner rig tested for 30 minutes without and with air cooling. Without cooling, the surface temperature reached 2350^0F. With cooling, the surface temperature decreased to 1910^0F, a drop of 440^0F. This demonstrates that silicon nitride is a candidate for cooled turbine components. **(Ram Bhatt, Jim Cawley, Ray Babuder, Dennis Fox (5160), and George Baaklini, Steve Arnold, Ali Aziz (all 5920))**

Space

Successful Operation of Silicon Nitride Ceramic Nozzle: In previous research on flat coupons at GRC it was demonstrated that silicon nitride is one of the few monolithic ceramic materials capable of surviving the severe thermal shock and thermal gradients generated in hydrogen/oxygen rocket engines. In-situ-toughened silicon nitride offers high strength, low density, and good thermal shock resistance. A one-inch diameter, in situ toughened silicon nitride rocket nozzle fabricated by rapid prototyping performed successfully in a rocket engine test stand, Cell 11, CRL. The thruster survived five cycles including a 10-min cycle to a >2400 °F material temperature. Compliant seals in the attachment area enabled installation of the nozzle without cracking. The nozzle survived five cycles including a five-minute duration cycle to 2400^{o}F material temperature. Silicon nitride can now be considered a viable candidate for some small rocket thruster applications. **(Andy Eckel, Jim Cawley, and Ray Babuder)**

Ablative Nozzle Materials Tests Support EELV: A number of rocket engine throat, nozzle and nozzle extension ablative materials were screened and post-test analyzed at GRC for the RS-68 Evolved Expendable Launch Vehicle (EELV). The testing was performed on a fully reimbursable basis in support of Thiokol and Boeing-Rocketdyne, under contract to the Air Force. The tests were performed in Cell 22 of the Combustion Research Laboratory, and were the fourth in a series of successful screenings. The tests enabled selection and development of economical, effective ablative nozzles. **(Ali Sayir, Andy Eckel, and Michael Harris)**

Light-Weight Gas Generator Combustor: A NRA 8-21 Light-Weight Gas Generator Combustor task proposed to introduce an alternative to conventional material usage for space transportation propulsion, in particular, RLV focused systems. The conceptual design phase has been reached with a CMC alternative for the gas generator combustor. A recent team review (GRC, MSFC, and Rocketdyne) has resulted in recommendations to be implemented into the sub-element conceptual design. Once modification of the conceptual design is complete, fabrication of the CMC based sub-elements can commence. This will then pave the way for hot-fire testing of the sub-element combustors. **(Jerry Lang, Andy Eckel, Jay Singh)**

Workshop on Carbon Fiber Reinforced Silicon Carbide for Space and Hypersonic Applications: Carbon fiber reinforced silicon carbide (C/SiC) is an important fiber reinforced ceramic matrix composite material for space transportation propulsion and vehicle hot structure applications. Personnel from NASA GRC, NASA MSFC, and the Air Force Research Laboratory at Wright-Patterson AFB organized a C/SiC workshop to identify key issues blocking systems applications. Forty-five people attended the workshop at GRC on May 6, 1999. They represented materials suppliers, NASA ARC and LaRC, technology facilitators, most major propulsion companies, and major airframe companies. The status of the technology was reviewed and major technical and programmatic issues were identified. Workshop results, in the form of a CR, will provide guidance for C/SiC development. (**Doug Kiser, Andy Eckel, and Stan Levine)**

Oxidation Model for C/SiC Composites: Analysis and further development of a finite difference model used for predicting the steady-state concentration of oxygen in a cracked carbon fiber / silicon carbide matrix (C/SiC) composite has been completed. The predicted steady-state oxygen concentrations obtained from the finite difference model compare very well with 1-dimensional and 2-dimensional analytical solutions based on mass transport theory. The model was advanced to include the removal of carbon during oxidation within a cross-section of a C/SiC composite. It allows for studies in oxidation kinetics where oxidized cross-sections that correlate to diffusion controlled and reaction controlled kinetics can be obtained. The effects on oxidation kinetics due to certain variables such as temperature, environment, diffusion coefficient, and reaction rate constant can be determined. **(Mike Halbig and Jim Cawley)**

C/SiC Database and Summarization of C/SiC Literature: C/SiC is an important ceramic matrix composite (CMC) material for space transportation applications. Therefore, researchers in France, Germany, Japan and the U.S. have been studying and documenting the processing, properties, microstructures, oxidation, failure analysis and applications of various types of C/SiC materials. A database of C/SiC literature has been prepared at GRC that currently includes over 140 documents, with these references categorized by subject and author. The intent of this effort, in part, is to develop and maintain a database so that information on current, state of the art, C/SiC research, as well as more mature processes, is readily available. The documents are currently being reviewed and a summary of C/SiC literature is being prepared. **(Paula Heimann)**

Microstructural Analysis of Melt Infiltrated C/SiC Mk-44 Stator Vane Subelements: Microstructural characterization of melt infiltrated (MI) carbon fiber reinforced silicon carbide matrix (C/SiC) Mk-44 stator vane subelements was performed for Boeing-Rocketdyne, to support their efforts in the IHPRPT "Low Cost C/SiC Composites by Melt Infiltration". Two different melt infiltration processes had been used in the fabrication of the stator vane subelements. The microstructures of four of these subelements were thoroughly characterized at NASA GRC. Comparisons of the microstructures of the two types of MI ceramic matrix composites were made. The results were used to correlate the effects of processing on subelement microstructure and mechanical behavior. **(Doug Kiser and Terry McCue (5120)**

Plasma Arc-Lamp Combustor Liner Durability Test System

J. C. Goldsby and M. C. Halbig

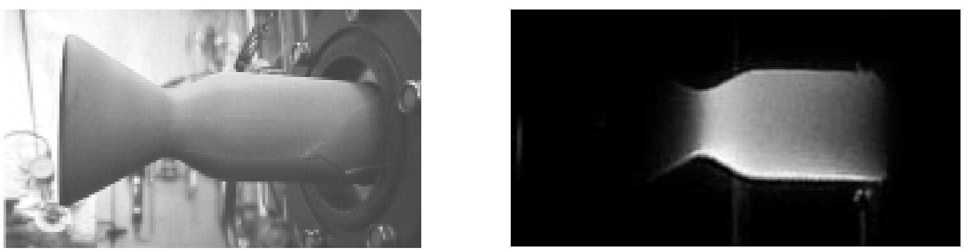
Silicon carbide matrix composites are candidate materials for high-temperature combustor liners. Combustor liners are primarily subject to stress due to through thickness thermal gradients. A unique test facility has been developed at NASA Glenn to simulate in-service pure thermal stress distributions in fiber reinforced silicon carbide cylinders. The facility was initially developed under the High Speed Research Program. To evaluate a combustor liner material's potential performance, thermal gradients are induced with an axisymmetric, direct current, electric arc within the cylinder while refrigerated air at a rate of 1.5 lb./sec impinges on the outside surface of the test cylinder. The achievable through thickness thermal gradient is predicted to be in excess of 200°C. The eight inch long and one half inch diameter plasma arc emits full spectrum visible light; radiant intensity exceeds 300 watts/cm^2 to produce temperatures in excess of 1500°C on materials with emissivity near unity. The test stand can accommodate test cylinders that are 4" in outer diameter, 8" in length and about 0.08"-0.12" in wall thickness. The cylinder is loaded vertically into the test stand. Water-cooled plates enclose the open ends of the cylinder and provide cooling. Load plates on the exterior side of the water-cooled plates provide support and compression surfaces. The system incorporates a standard mechanical test frame, which can impose constant as well cyclical axial stresses up to 2200 pounds upon the test piece. The cylinders will be instrumented to obtain through thickness thermal flux measurements and to obtain the resulting stress distribution throughout the sample. One of the special features of this configuration is the creation of hoop stress states within the cylinder, which up this point were not obtainable in planar coupon tests. In addition because the system does not rely upon the combustion of fuels to achieve the related thermal conditions, ancillary environmental reactions with the sample are eliminated. This facility will allow various operational modes, which include accelerated tests of thermal transients simulating the effects of repeated engine ignition as well as prescribed thermal and mechanical histories to simulate various duty cycle profiles. Tests may now be performed on thermal barrier coated metallic liners and ceramic composite liners that require a combination of high heat flux and controlled mechanical stresses.

Silicon Nitride Rocket Thrusters Successfully Test Fired

A. J. Eckel

In-situ toughened silicon nitride offers high strength, low density, and good thermal shock resistance. In previous research on flat coupons at GRC, it was identified as one of the few monolithic ceramic materials capable of surviving the severe thermal shock and thermal gradients generated in hydrogen/oxygen rocket engines. To demonstrate the capability in a complex configuration, one-inch diameter, single-piece combustion chamber/nozzle (thruster) components were fabricated using advanced rapid prototyping technology. The net shape fabricated uncooled thruster was attached to a water-cooled metallic propellant injector assembly using compliant seals. The thruster was successfully hot-fire tested using hydrogen/oxygen propellant. The thruster survived five cycles including a five-minute duration cycle to a 2400^{o}F material temperature. Silicon nitride can now be considered a viable candidate for some small rocket thruster applications.

A team from NASA Glenn Research Center, and Case Western Reserve University conducted this research. The research is expected to continue with increasingly larger and more complex geometries being fabricated and tested in a broad range of rocket engine operating conditions.



(a) (b)

Silicon nitride thruster (a) mounted in test stand, (b) being tested with H_2/O_2 propellants.

Affordable, Robust Ceramic Joining Technology (ARCJoinT) Wins 1999 R&D 100 Award

M. Singh

Advanced ceramics and fiber-reinforced ceramic matrix composites with high strength and toughness, good thermal conductivity, thermal shock resistance, and oxidation resistance are needed for high-temperature structural applications in advanced high-efficiency and high-performance engines, space propulsion components, and land-based systems. The engineering designs of these systems require the manufacturing of large and complex shaped parts, which are either quite expensive or impossible to fabricate. In many instances, it is more economical to build up complex shapes by joining together simple geometrical shapes. Thus, joining has been recognized as an enabling technology for successful utilization of advanced ceramics and fiber reinforced composite components in high temperature applications. However, the joints must retain their structural integrity at high temperatures and must have mechanical strength and environmental stability comparable to the bulk materials. In addition, the joining technique should be robust, practical, and reliable.

ARCJoinT, which is based on the reaction forming approach, is unique in terms of producing joints with tailorable microstructures. The formation of joints by this approach is attractive since the thermomechanical properties of the joint interlayer can be tailored to be very close to those of the base materials. In addition, high temperature fixturing is not needed to hold the parts at the infiltration temperature. The joining process begins with the application of a carbonaceous mixture in the joint area, holding the items to be joined in a fixture, and curing at 110-120°C for 10 to 20 minutes. This step fastens the pieces together. Then, silicon or a silicon-alloy in tape, paste, or slurry form is applied around the joint region and heated to1250-1425°C (depending on the type of infiltrant) for 10-15 minutes. The molten silicon or silicon- refractory metal alloy reacts with carbon to form silicon carbide with controllable amounts of silicon and other phases as determined by the alloy composition. Joint thickness can be readily controlled in this process, by controlling the properties of the carbonaceous paste and applied fixturing force. ARCJoinT received R&D Magazine's prestigious R&D 100 Award in 1999.

Thermomechanical and thermochemical characterization of joints in a wide variety of silicon carbide based advanced ceramics and fiber reinforced composites under the hostile environments that will be encountered in engine applications is underway.

Directionally Solidified Ceramics

S. C. Farmer and A. Sayir

Multiphase, interpenetrating structures are an alternative route to obtaining structural ceramic materials with adequate strength, toughness, and stability for high temperature aerospace applications. The eutectic architecture, a continuous reinforcing phase within a higher volume phase or matrix, can be described as a naturally occurring *in-situ* composite. The phases of a eutectic are thermodynamically compatible at high homologous temperatures. Strong and stable materials have been produced. Toughness, however, remains a technical obstacle. The potential for producing enhanced toughness materials of adequate strength and stability has been demonstrated using the LHFZ (laser-heated float zone) growth method.

Laser heated float zone (LHFZ) growth at NASA Glenn provides a means to efficiently produce and record the underlying growth phenomena associated with two-phase structures. To initiate directional solidification, a seed of single crystal sapphire (<0001> direction) was lowered onto the molten liquid until wetting occurred and is then withdrawn at a constant rate. Neither the crystal nor the source rod was rotated. Materials produced were mechanically tested in tension and microstructure was examined using scanning electron microscopy.

Both the inherent properties of the constituent phases and the properties of the interface between them affect the mechanical behavior. A flat fracture surface is typical of a strong, but low toughness material. Cracks are effectively deflected at the interface between the two phases achieving higher toughness at moderately lower strength levels. Mechanical tests to determine high temperature properties of these materials is the next step in determining their eventual suitability.

CONSTITUENT-BASED LIFE MODELS FOR SiC/SiC COMPOSITES

J. A. DiCarlo and H. M. Yun

The successful utilization of ceramic matrix composites (CMC) as hot-section components in advanced aeropropulsion engines will require tailoring and optimization of the CMC constituents in order to meet all the critical property demands of each component. Under the High Speed Research and Advanced High Temperature Engine Materials Technology Programs, research efforts have been initiated at GRC to develop mechanistic models which describe the effects of different constituent factors (composition, geometry, volume fraction) and of potential application conditions (stress, time, temperature, environment) on key CMC thermostructural properties. Particular focus has been placed on both analytical and computer modeling of state-of-the-art SiC/SiC composites where the primary load-bearing constituents are stoichiometric SiC fibers in a complex multiphase SiC matrix produced by chemical vapor infiltration and melt infiltration.

Besides developing computer models for the elastic modulus, thermal expansion, and thermal conductivity properties of the SiC/SiC system [1], recent studies have also generated analytical models for the time dependence of composite rupture strength at temperatures above 2200^{o}F (1200^{o}C) where CMC have an important thermostructural advantage over current nickel-based superalloys. These life models utilize thermal activation theory and fiber stress-rupture results measured at GRC in order to generate Larson-Miller (LM) plots of fiber rupture strength versus **q**, a single time/temperature-dependent parameter [2]. Assuming a worse case in which the SiC matrix is cracked, rupture is then controlled by the time-dependent fracture characteristics of the fiber bundles bridging the matrix cracks. With this as the controlling mechanism, one can then use simple composite theory and the fiber LM plots to predict CMC rupture strength versus the q parameter [3].

To generate our predictions, a 2-dimensional 0/90 composite with ~16% fiber in the applied stress direction and an air test environment were assumed. As such, it is possible to compare the model predictions against limited strength data for this CMC. The good agreement confirms the rupture model at least for the selected CMC and test conditions. Thus for this particular SiC/SiC composite, one can estimate a 1000-hr rupture strength of ~12 ksi at 2400^{o}F (T = 1588 kelvin and q = 39700 kelvin). At lower CMC application stresses, the SiC matrix is typically uncracked so that both the fiber and matrix constituents share the composite load. In this case, CMC rupture will be controlled by the constituent with the longest rupture time based on the creep rate of the composite. By using measured Monkman-Grant plots of rupture time versus creep rate for the two SiC constituents, CMC life models for this important application condition have also been developed [4]. NASA and DOD are currently using this information to establish application and materials goals for more advanced CMC with higher temperature capability.

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Tribology and Surface Science Branch
(5140)

Oil-Free Turbo Machinery (C. DellaCorte, J. Lucero, M. Valco, K. Radil, T. Zaldana, V. Lukaszewicz, M. Stanford)
- Dynamic Face Seal Arrangement - One of the last patents of the Millennium
  - Nominated for 1999 Inventor of the Year Award

Space Lubrication (W. Jones, S. Pepper, M. Jansen, Q. Nguyen, D. Dixon, E. Kingsbury, R. Price, W. Morales)
- Oozing-flow lubricated bearing cartridge & Kevlar-carbon-composite momentum wheel
  - Now commercially available for momentum wheels and gyroscopes in future satellites
- Rehab of Space Tribometer Facility
  - State-of-the-art facilities available for other NASA Centers and industry
- Developed method for applying thin ceramic coatings on ball bearings
  - Will replace tricresyl phosphate (a toxic material) procedure

Vapor Phase Lubrication (W. Morales, R. Handschuh)
- Vapor phase lubrication spur gearbox fitted with sensors
  - Baseline testing completed
- NASA Exceptional Service Medal (Wilfredo Morales)

Computational Materials *AKA Atomistic Modeling* (G. Bozzolo, J. Ferrante, P. Abel, F. Honecy, B. Goode, R. Noebe)
- "Surface Segregation in Multicomponent Systems" published in Special Review Issue of *Computational Materials Science*
  - Selected for Best Paper of Materials Division in 1999
  - NASA Group Achievement Award

MEMS Tribology Group *AKA Micro Machinery* (P. Abel, K. Miyoshi, W. Mueller, K. Street, W. Morales, C. Navarro)
- Receives first funding for MEMS research from JPL
  - GMI funding still under negotiation
- Electrochemical Cell for production of porous silicon constructed
  - A new mechanism for elimination of stiction

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Computational Modeling of Fluid Bearings (D. Brewe)

- Tribological Components - Slider Bearings
  - A major chapter in the CRC Handbook of Modern Tribology

Fiber/Matrix Interface Testing (J. Eldridge)

- BN-coated fibers show significant short term effects of humid-air on sliding behavior

IR Microspectroscopy (K. Street, P. Griffin)

- Egyptian Antiquities from the Cleveland Museum of Art analyzed
  - Understanding of the construction methods of the artisan and for restorative purposes

Technology Transfer (W. Morales)

- New and inexpensive, environmentally friendly non-chromate phosphate coating method developed
  - Space Act Agreement initiated for commercialization

Computational Modeling of Surface Alloys

G. Bozzolo and P. Abel

The formation of surface alloys is a growing field which, in terms of surface structure of multi-component systems, defines the frontier both for experimental and theoretical techniques. Due to the impact on surface properties that the formation of a surface alloys has, it is necessary to establish reliable methods to aid in the prediction of new surface alloys or to allow researchers to interpret unknown structures. The structure of surface alloys, when and even if they form is largely unpredictable based solely on known properties of the participating elements. No unified theory or model to date can infer surface alloy structures based on the constituents properties or their bulk alloy characteristics. In spite of these severe limitations, a growing catalogue of such systems has been developed during the last decade and it is only recently that global theories are being advanced to fully understand the phenomenon.

In terms of modeling, none of the available methods used in other areas of surface science are capable of properly dealing even with the already known cases. Aware of these limitations, the Computational Materials Group (CMG) at Glenn Research Center has developed a useful, computationally economical and physically sound methodology to enable the systematic study of surface alloy formation in metals. This tool has been successfully tested on several known systems for which hard experimental evidence exists [1,2], and has been also used for the prediction of ternary surface alloy formation [3], a field yet to be fully explored experimentally.

The computational tool, based on the BFS method for the calculation of the energetics, consists of a small number of simple PC-based computer codes which deal with the different aspects of surface alloy formation. Two analysis modes are available within this package. 1) An atom-by-atom description of real and virtual stages during the process of surface alloying based on the construction of catalogues of configurations where each configuration describes one possible atomic distribution. A BFS analysis of this catalogue provides information on accessible states, possible ordering patterns, details on island formation or film growth and, more importantly, provides insight on the evolution of the system. Software developed by the CMG allows for study of an arbitrary number of elements forming surface alloys, including also an arbitrary number of surface atomic layers. 2) Large scale temperature-dependent computer simulations, using the BFS method for the energetics, that provide information on the dynamical processes during surface alloying. These simulations require the implementation of Monte Carlo based codes with high efficiency within current workstation environments.

The methodology introduced capitalizes on the advantages of the BFS method: there are no restrictions in the number or type of elements or the type of crystallographic structure considered. This removes any restrictions in the definition of the configuration catalogues used in the analytical calculations, thus allowing for the study of arbitrary ordering patterns, ultimately leading to the actual surface alloy structure. Moreover, the Monte Carlo numerical technique used for the large scale simulations allows for a detailed visualization of the simulated process, the main advantage of this type of analysis being the ability to understand the underlying features that drive these processes. At any point in the simulation, a detailed atom-by-atom analysis can be performed, due to the simplicity of the BFS method for energetics used in these calculations, providing necessary insight on the details of the process.

The main objective in this research program consists of developing a useful tool for the experimentalist to guide understanding and interpretation of often unexpected results in alloy formation experiments. By reducing the computational effort without losing physical accuracy, it is expected that powerful simulation tools will be developed in the immediate future which will allow material scientists to easily visualize and analyze processes at a level not achievable experimentally.

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1999 Technical Accomplishments and Highlights
Polymers Branch - 5150

Reduce component costs through the development of affordable, processable, environmentally friendly polymers for 550°F (290°C) applications

- Continued development of new, non-toxic replacements for PMR-15 (BAX, Bis-M and Bis-P) (Ray Vannucci, Peter Delvigs, Dan Scheiman, DeNise Hardy-Green)
  - ✓ Leading resin candidate is BAX polyimide, developed by GRC under the AST program - has the best combination of processability, stabiltiy and high temperature performance
    - Diamine precursor is not comercially available, and is costly to synthesize by current route
    - Under SBIR contracts with Maverick Corporation (Phase II) and Triton Systems (Phase I) have developed a low-cost commercializable route to BAX diamine, Maverick is scaling their process up to 10Kg for the UEET Program
    - Transitioning BAX polyimide to the UEET program
  - ✓ Bis-M and Bis-P resins, developed by Maverick, are prepared from commercially available diamines and show promise as PMR-15 replacements
  - ✓ Working with St. Norbert College to investigate other non-toxic diamines for use in high temperature polyimides, identified several new fluorinated diamines that give negative Ames' test (non-mutagenic) and afford polyimides and composites with stability and performance equivalent to PMR-15
- Continued efforts to develop new polyimide resins with low melt viscosities that can be processed by cost effective methods, e.g., Resin Transfer Molding. Industry experience shows that RTM processing lowers component manufacturing costs by 30 to 50% over hand lay-up based processing methods. (Chris Gariepy, Baochau Nguyen, Mike Meador)
  - ✓ RTM processable polymers for 550 to 700°F (290 to 370°C) cited as major industry, NASA, and DoD need (Aero and Space)
  - ✓ Completed DOE (Design of Experiments)-based studies on two new approaches to processable polyimdes- star-branched systems and "twisted bi-aryls". Results suggest that both systems hold promise for RTM processing.
  - ✓ Purchased new RTM system with support from UEET program - should be delivered to GRC within the next few weeks
  - ✓ Exploring applications and new RTM processable materials under HOT PC, RLV Focused Technology programs and a Boeing/NASA GRC, LaRC RLV activity
- Exploring other processing approaches to reduce component manufacturing costs (Ray Vannucci, Maverick Corp., GEAE, Canyon Composites, Fiber Innovations)
  - ✓ Extending applications for Solvent Assisted Resin Transfer Molding (saRTM), developed by Fiber Innovations, GEAE and GRC, to primary aircraft engine components (UEET) and RLV components (ducts and propulsion components).
  - ✓ Investigating other approaches to infiltrating/processing braided structures (joint with Canyon Composites)

- ✈ Investigating cure chemistries of new materials and developing methods to improve their storage life, to enhance component quality and improve processing reliability. (Chris Johnston, Bill Alston, Dan Scheiman)
  - ✓ Developed a simple, accurate method to measure diamine reactivity based upon ^{15}N nmr spectroscopy. This technique will enable the estimation of diamine reactivity and understand aspects of resin processing kinetics from a few milligrams of compound.
  - ✓ Applied PMR Extended Shelf Life approach to improving the solution stability of BAX and DMBZ resins. Use of this approach enables the shipment and storage of resin solutions used in the saRTM process.

- ✈ Developing new polyimide resins for 550°F (290°C) use that can be cured with radiation (e-beam or ultraviolet light) rather than heat. (DeNise Hardy-Green, Sandi Campbell, Mike Meador, KSU)
  - ✓ Radiation curing can lead to reduced processing temperatures, tooling costs, and processing times as well as enable the fabrication of structures too large to be processed by conventional methods (autoclave processing)
  - ✓ Major need for RLV program - fabrication of composite LOX and LH2 tanks
  - ✓ Initiated Cooperative Agreement with Kent State University for resin development and access to their new electron beam site (NE Ohio Beam Alliance in Middlefield, OH).
  - ✓ Exploring other resin chemistries at GRC.
  - ✓ Funding an SBRI contract with Adherent Technologies (Phase I) to pursue other chemstries

- ✈ Exploring new resin chemistries for potential use as hot-melt adhesive adhesives for RLV cryotank and airframe structures applications (Kathy Chuang, Demetrios Papadopoulos, U of Akron, U of Western Kentucky)
  - ✓ Processable, high flow adhesives for bonding large structures, i.e., cryotanks for RLVs, are a major NASA, DoD, industry need
  - ✓ Developing several new formulations in-house
  - ✓ Revived adhesive testing and processing capability at GRC
  - ✓ Characterizing materials at U of Akron and U of Western Kentucky

Continuing efforts to understand the degradation mechanisms and durability of polymers and composites at high temperatures and explore methods to enhance their survivability at high temperatures

- ✈ Exploring the mechanical behavior of fiber reinforced polymer matrix composites at temperatures well above "typical" upper limits (Kathy Chuang, Ken Bowles, Demetrios Papadopoulos, Jim Sutter, Rod Ellis (5920), Mike Castelli (5920/OAI), Cheryl Bowman (5920/OAI)
  - ✓ Demonstrate that stitched carbon fabric reinforced DMBz-15 composites survived a 15 minute simulated mission profile to 1000°F
  - ✓ Investigated the TMF behavior of PMR-II-50 and AFR-700B composites at temperatures 200°C higher than their "typical" use temperatures.
- ✈ Examining the response of polymeric materials to high strain energy release rate events, e.g., ballistic impact. This information can be used to design more efficient materials and designs for lightweight containment systems for aircraft engines, turbopumps, and flywheels. (Gary Roberts, Mike Periera (5920), Norton Performance Plastics)

- ✓ Performed ballistic impact tests on ceramic/PMC layered panels. Results demonstrated that a ceramic front layer can be used to prevent fiber cutting on the PMC surface when impacted by a titanium projectile. (Collaboration with Norton Performance Plastics, Ravenna, Ohio)
- ✓ Performed quasistatic and split Hopkinson bar tests to measure the tensile properties of 977-2 epoxy resin at strain rates from 0.0001/s to 1000/s. Results demonstrated an increase in modulus at high strain rates. Further analysis of the split Hopkinson bar data resulted in recommendations for improving the design of polymer resin specimens used in the test. (Collaboration with Dr. Rob Goldberg/5920 and Prof. Amos Gilat/Ohio State University)

- ✈ Established a new biaxial test facility to measure the mechanical responses of polymers and elastomers to finite strains over typical use temperature ranges. This data will be used to verify mathematical models for the viscoelastic and viscoplastic responses of these materials that are being developed under the Ultrasafe program. Materials testing will begin in 2000 in a collaborative activity with the U of Akron Department of Polymer Engineering(Al Freed)
- ✈ Initiated research program in the development of polymer/aluminosilicate nanocomposites for use in aerospace components. Research by other groups has shown that these nanocomposites have improved toughness and tensile strength, increased thermal oxidative stability, and reduced gas permeability than comparable base polymers. Several PMR-15 nanocomposite formulations have been prepared and their mechanical behavior, gas permeability, and long term thermal oxidative stability is under evaluation. These materials are under investigation for use in LH_2 tanks and feedlines for the RLV and Zero CO2 Emissions programs, and as a means of improving the thermal oxidative stability of high temperature resins under the HOT PC program. (Sandi Campbell)
- ✈ Defined thermal degradation mechanism of Hubble Space Telescope aluminum coated fluoropolymer multi-layer thermal insulation from Servicing Missions 1 & 2. (Jim Sutter, Electrophysics Branch.).

Continually upgrade and enhance processing, characterization, and testing facilities to maintain world-class capabilities in Polymers and support current and future NASA programs.

- ✈ Upgraded Branch processing equipment through the installation of a Windows based control and data (temperature, pressure, time) collection system. This will improve the reproducibility of processing cycles developed for advanced polymeric materials (Chris Johnston, DeNise Hardy-Green, Howard Eakin (7290))
- ✈ Purchased a new high temperature Resin Transfer Molding facility to enhance the Branch's processing capabilities to address emerging needs in Space (RLV, Spaceliner) and Aeronautics (HOT PC, UEET). (Demetrios Papadopoulos)
- ✈ Upgraded the Polymers Branch long-term aging ovens through the installation of a computer based temperature control/monitoring system. (Demetrios Papadopoulos, Jim Sutter, Howard Eakin (7290), James Williams (7290))
- ✈ Purchased a new automated prepreg winder to support composites processing work in HOT PC, UEET, Zero CO2 Emissions, Spaceliner and RLV programs. (Kathy Chuang, Howard Eakin, Dan Scheiman (Dynacs)

Development of Erosion Coatings for High Temperature Polymer Composites: A Collaborative Project with Allison Advanced Development Company

J. K. Sutter

The advantages of replacing metals in aircraft turbine engines with high temperature polymer matrix composites (PMCs) include weight savings accompanied by strength improvements, reduced part count and lower manufacturing costs. Successfully integrating high temperature PMCs into turbine engines requires several long-term characteristics. Resistance to surface erosion is one rarely reported property of PMCs in engine applications because PMCs are generally softer than metals and their erosion resistance suffers. Airflow rates in stationary turbine engine components typically exceed 2.3 kg/sec at elevated temperatures and pressures. In engine applications, the survivability of PMC components is clearly a concern, especially when engine and component life-cycle requirements become longer.

Although, very few publications regarding the performance of erosion coatings on PMCs are available–particularly in high temperature applications–the use of erosion resistant coatings to significantly reduce wear on metallic substrates is well documented. In this study, a low cost [at less than $140/kg] graphite fiber reinforced T650-35/PMR-15 sheet molding compound (SMC) was investigated with various coatings. This SMC has been compression molded into many structurally complicated components, such as shrouds for gas turbine inlet housing and gearboxes. Erosion coatings developed for PMCs in this study consisted of a two-layered system: a bondcoat sprayed onto a cleaned PMC surface followed by the application of an erosion resistant, hard topcoat sprayed onto the bondcoat. A total of 6 erosion coating systems were evaluated for their ability to withstand harsh thermal cycles, erosion resistance (*ASTM G76-83 Standard Practice For Conducting Erosion Tests by Solid Particle Impingement Using Gas Jets)* using Al_2O_3, and adhesion to the graphite fiber polyimide composite (*ASTM D 4541-95 Pull Off Strength of Coatings)*.

NASA Glenn and Allison Advanced Development Company collaborated to optimize erosion coatings for gas turbine fan and compressor applications. All of the coating systems survived aggressive thermal cycling without spalling. During erosion tests, the most promising coatings systems tested were with Cr_3C_2-NiCr and WC-Co as the hard topcoats. In all cases, these coating systems performed significantly better than the hard topcoat TiN. When material depth (thickness) loss is considered, the Cr_3C_2-NiCr and WC-Co coating systems provided on average, 8.5 times greater improvement in erosion resistance as compared with uncoated PMR-15/T650-35 composite. Similarly, Cr_3C_2-NiCr and WC-Co coating systems adhered to the PMC substrate during tensile tests significantly better than systems containing topcoat TiN. To determine differences in topcoats Cr_3C_2-NiCr and WC-Co, issues such as cost and environmental impact were considered. The preferred erosion resistant coating system for PMR-15/T650-35 is WC-Co as the hard topcoat. This system provides the following benefits when compared to the coating system with Cr_3C_2-NiCr topcoat: lower powder material cost (15-20%), environmentally friendly materials (Cr_3C_2-NiCr is hazardous), and higher deposition yield (10-15%) which results in less waste.

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Extended Shelf Life for PMR Polyimide Monomer Solutions and Prepregs

W. A. Alston and D. A. Scheiman

PMR (Polymerization of Monomeric Reactants) technology was developed in the mid 70's at the NASA-Glenn Research Center (GRC) for use in fabrication of high temperature stable polyimide composites. This technology allowed a solution of polyimide monomers or a prepreg (a fiber, such as glass or graphite, impregnated with PMR polyimide monomers) to be thermally cured without the release of volatiles that cause the formation of voids; unlike the void formation typically experienced in non-PMR technology condensation polyimide resins. The initial PMR resin introduced as PMR-15 is still commercially available and used worldwide by aerospace industries as the state-of-the-art resin for high temperature polyimide composite applications. PMR-15 offers easy composite processing, excellent composite mechanical property retention, a long lifetime at use temperatures of 500-550 °F and relatively low cost. Later versions of PMR resins, e.g. PMR II-50 and VCAP-75, offer improvements in upper use temperature (to 700 °F) and useful life at temperature without major compromises in processing and property retention but with significant increases in resin cost.

Unfortunately all PMR polyimide solutions and prepregs suffer from a common problem of a short shelf life. State-of-the-art PMR-15 has a maximum of three weeks at room temperature storage or shelf life. Newer versions of PMR monomer solutions and prepregs exhibit an even shorter shelf life over an order of magnitude less than the state-of-the-art PMR-15. This short shelf life problem has plagued industry since PMR's inception until now. Researchers at GRC discovered that the PMR shelf life is dramatically improved by a modification using secondary alcohols (preferably isopropanol) to both esterify the PMR monomer mix and as the solvent instead of conventional primary alcohols (methanol or ethanol). In-house researchers also found that PMR monomer solutions and prepregs made with this alternative ester approach are less reactive during comparable storage and handling temperatures without affecting typical curing temperatures. In some cases a thirty-fold increase in shelf life was observed before the PMR-15 solution forms precipitates.

This method of improving PMR shelf life could offer several advantages over conventional PMR technology because of its wider tolerance to temperature or mishandling of solutions and prepregs. These advantages translate into reduced shipping and handling costs by eliminating the need for refrigeration, reduced variability between PMR monomer batches that results in more consistent processability, improved hot-melt PMR prepreg manufacturing, reduced scrap rates, improved safety from use of less toxic isopropanol (compared to methanol and ethanol) and improved adaptability to some processing techniques such as Solvent Assisted Resin Transfer Molding (SaRTM). Further work is ongoing to exploit all these advantages.

Resin Transfer Moldable Polyimides for High Temperature Applications

M. A. Meador, C. Gariepy, and M. A. Meador

High temperature polyimides, such as the GRC developed PMR-15, are becoming an increasingly important class of materials for a variety of aerospace applications, such as aircraft engine components, and propulsion and airframe components for reusable launch vehicles (RLVs). Because of their high specific strength and low density, use of these materials in place of more traditional aerospace materials, such as titanium, can significantly reduce component and vehicle weight leading to reductions in fuel consumption (and pollutants), increases in payload/passenger capacity, and improvements in vehicle performance.

Typical methods for fabricating components from these high temperature materials are fairly labor intensive and costly. More cost effective methods, such as Resin Transfer Molding, RTM, have been developed and successfully employed with low temperature polymers (use temperatures no higher than 400°F). Use of RTM processing can lead to as much as a 50% reduction in manufacturing costs over traditional fabrication methods. In the RTM technique a preform, made by weaving or braiding fiber reinforcements, is infiltrated with molten polymer and the resulting structure cured at elevated temperatures. In order to successfully fill the mold and wet out all of the fibers in the preform, the molten polymer must have a melt viscosity no higher than 1000 centiPoise, about the consistency of castor oil. High temperature polymers, such as PMR-15, have melt viscosities on the order of 200,000 centiPoise - the consistency of peanut butter. The challenge is to develop new polymers that have melt viscosities low enough to enable RTM processing and that have the stability and high temperature properties necessary for operation at temperatures above 450°F (232°C).

A recent collaboration between researchers in the Polymers Branch and the University of Akron's Institute of Polymer Science has led to the development of a new family of PMR polyimides with melt viscosities low enough for RTM processing. Melt viscosities of these imide oligomers were measured by pressing 0.5 grams of resin powder between two 12"x12" sheets of Kapton in a heated press (500°F, 260°C) at 170 psi pressure. Areas of the resulting resin "splots" (Squeeze Flow Index) were measured as a function of formulated molecular weight. Those resins with Squeeze Flow Indexes greater than 220 cm^2 have melt viscosities below 1000 centiPoise. Most of the resins prepared from BAPP and BAX diamines have melt viscosities low enough for RTM processing. Neat resin samples were molded from these imide oligomers at 316°C and post-cured for 16 hours at 325°C. Weight losses for these samples after 250 hours of aging in air at 550°F (290°C) were determined. Resin samples prepared from the BAX diamine showed the lowest weight losses of all samples tested and suggest good long-term stability at or near 550°F. Further work is underway to evaluate these materials in carbon fiber reinforced composites.

Environmental Durability Branch

Technical Accomplishments for 1999

METALS

- Established the oxidative behavior of Cu and Cu alloys via thermogravimentric analysis from 600-800^{o}C.(Thomas-Ogbuji, Humphrey)
- A no bond coat plasma-sprayed thermal barrier coating over high sulfur single crystal PWA1484 alloy exhibited spallation failure after 200 hr, at 1100^{o}C, whereas a hydrogen annealed sample produced 5x improvement in life under the same test conditions. (Smialek, Leissler, Humphrey, Cuy)
- Demonstrated ability of evaporated alpha-alumina film to effectively eliminate diffusion between a superalloy and overlay coating after 1200^{o}C exposure for 100 hr. (Nesbitt, Humphrey, Kostyak, 5510)
- About 40 promising ternary and quaternary active element additions to NiAl have been processed and tested at GEAE (SAA3-196) with the goal of developing new NiAl-based bond coats with increased temperature capability. Very long test lives have been observed for three of the compositions studied. (Miller, Zhu, Noebe, Bowman, Hebsur)
- Oxidation and corrosion burner rig studies of coated and un-coated vane doublets, 1650 hrs at 1950^{o}F, was completed, enabling final selection of the GP-275 coating for the Williams' General Aviation turbine engine development. (Fox, Cuy)
- A modelling package, which integrates the COSP model (aluminum oxide growth and loss) with a finite difference model of the inter-diffusion of elements between a coating and substrate, has been developed. The new model can predict life enhancements due to the use of diffusion barriers. The model is already in the hands of several of our customers. (Nesbitt)
- Approximately 11 million thermal HCF cycles and 200-30min heating/cooling cycles have been completed for each of the stainless steel and Haynes 188 specimens at 30 Hz enhanced laser pulse frequency under study for the Pulse Detonation Engine project. Preliminary failure mechanisms have been identified. (Zhu, Miller)

POLYMERS

- Endcap degradation in PMR polyimide resins accounts for much of the weight loss during aging, in air, at elevated temperatures. Carbon-13 tagging made possible the identification of major degradation pathways. New composition studies have identified promising chemistries, which should favor a reaction path yielding more stable oxidation products. Reductions in PMR weight loss can prolong the lifetime of polymers. (Mary Ann Meador)

- Oxidation of PMCs at high temperatures can be slowed through the use of protective coatings, but maintaining adhesion has been difficult. PMC substrates, which have been fabricated and coated with different interface and top coatings, have just completed thermocycling (between room temp and 300^{o}C) for up to 300hrs. Thermo-oxidative stability and adhesion improvements are being evaluated.(M.A.B.Meador, G. Leissler)

CERAMICS

- Completed 200 hour HPBR durability testing and exposure effects on microstructural scale formation/stability on the high priority EBC coatings. (Lee, Robinson, Opila, Smialek)
- Completed two-part test series on CMC inserts for leading edge protection of stage two, high pressure turbine nozzle guide vanes for the Pegasus engine in support of an Office of Naval Research (SAA3-145)effort with Allied Signal Composites, Inc. Approximately a 600^{o}F reduction in the internal metallic vane was achieved. (Robinson)
- Completed computational and experimental studies of advanced phase change materials for aircraft system application through OAI and company interaction (SAA3-202). (Opila)
- Completed 150 hr burner rig oxidation study of Sylramic-reinforced and Hi-Nicalon reinforced fiber/BN/SiC composites. Significant CMC strength degradation and severe internal oxidation was seen at the interface. A carbon film(PEO fiber burn-off) was observed and fibers were heavily damaged through oxidation. (Thomas-Ogbuji, Cuy)
- Provided short cycle exposures of ceramic radomes at 635^{o}F for the Sparrow missile, fabricated by Composite Optics, Inc. The objective was to assess changes in the circuit integrity of the radome due to elevated temperature exposure. (Angel, Cuy)

- TBC coated metal combustor mini-segments were run for 125 hours under laser heating in the 6 atm test chamber. The effect of aging on thermal conductivity, surface cracking, creep strain, modulus and other key properties were evaluated. (Fox, Miller, Zhu)
- Demonstrated application of Raman microscopy to map regions of stress relief associated with delamination of thermal barrier coatings. (Eldridge)
- Completed characterization study of the coefficients of friction and wear rates of ion-plated lead, magnetron sputtered and chemical vapor deposited diamond-like carbon films in ultra high vacuum, dry nitrogen, and humid air. The lead films met the performance requirements only in space-like vacuum, while the DLC met them in both air and nitrogen. (Miyoshi)
- Reaction kinetic studies of silicon nitride (CVD, AS800 and SN282) were studied at temperatures between 1200^o and 1400^{o}C, in 50% water vapor - 50% oxygen environment. All materials exhibited parabolic kinetics, confirming that silicon nitride reacts similarly to silicon carbide, volatilization of the protective silica scale with accelerated consumption of the material. (Fox, Opila, Humphrey, Nguyen, Lewton)
- One-thousand hour burner rig exposures were conducted demonstrating that the mullite/YSZ coating systems, while promising coatings for melt-infiltrated SiC composites, performed poorly on chemical vapor infiltrated SiC composites (DuPont standard and enhanced SiC/SiC). Cracking and spallation takes place due to thermal expansion mismatch and phase transformation of precipitates in the mullite. (Fox, Lee, Cuy)
- A new application for vacuum-assisted forming to produce large, complex, near net-shaped parts was demonstrated of cemented tile joints are major improvements to the current methods. (Angel)
- Completed both a rhenium oxidation study and a study of the thermal fracture behavior and failure mechanisms of various single crystal oxides to determine the best material for a refractive secondary solar concentrator application. (Jacobson, Zhu, Humphrey)
- Computational thermodynamics and experimental studies were conducted to identify the chemical degradation mechanisms responsible for the Hypersonic Tunnel Facility (HTF) failure incident. Recommended operational procedures for bringing the huge graphite induction furnace to test temperatures were instituted. Monitoring water vapor and selected gaseous by-products was implemented in the testing protocol. (Jacobson)

FACILITIES AND TECHNIQUES

- Enhanced measurement sensitivity and analyses efficiency has been achieved in the High Temperature Mass Spectrometer through the design, development and implementation of an automated data acquisition and peak analysis code. (Auping, Jacobson)
- A laser-heated 4-point bend test was developed for testing Caterpillar diesel engine coatings under combined thermal and mechanical fatigue and to evaluate EBCs on CMC combustor materials in cooperation with NC A&T State Univ. (Miller, Zhu, Calomino)
- Dual-gun PVD system modifications were completed, improving the quality of the vacuum achievable and increasing the size/configuration options for substrates. (Kostyak, Nesbitt)
- Introduced new hot erosion testing capability in Mach 0.3 burner rig (Cell 125) for EPM exhaust nozzle and superalloy mixer materials. (Cuy, Lee) Minor modifications for testing erosion resistant coatings on PMCs are underway. (Cuy, Miyioshi)
- Installed a minor production spray drying system to fabricate unique ceramic powders for thermal barrier coatings research. (Miller, Zhu, G. Leissler, S. Leissler, Setlock)
- The laser thermal conductivity/sintering technique, originally developed for YSZ coatings on superalloys, has been adapted to allow evaluation of a wide variety of coated and uncoated materials, including alternate TBCs, EBCs, free-standing ceramics, and NiAl. (Miller, Zhu)
- Developed instrumented Vickers micro-indentation testing for the determination of elastic modulus gradients within thermal barrier coatings. (Eldridge)
- A new transpiration furnace was designed and assembled for measuring high temperature thermodynamic property data. Such data is key to our computational efforts, predicting chemical reactions and material compatibility. (Jacobson, Copeland, Opila, Myer)

SPECIAL HONORS

- Successful transfer of the HSR environmental barrier coatings technology to DOE’s land-based turbine applications. Long-term testing of the coated CMC composite is underway at Solar Turbines, Inc. in a Centaur 50S turbine engine. The material system has provided protection for 6000 hr, with continuing testing underway toward the 8000+ hours life goal. (Lee, et. al. With HSR - EBC and CMC Team members)

- Nathan Jacobson was named Fellow in ASM International
- Michael Cuy was featured in the December 1999 issue of Sport Aviation, Vol. 48, No. 12, “The Pietenpol Air Camper 70 and Counting,” pp41-54, by J. Cox, which described the building of his personal plane, which he now flies to the OSHKOSH Air Show.
- Paper “Key Durability Issues with Mullite-Based Environmental Barrier Coatings for Si-Based Ceramics,” was recognized at the American Society of Mechanical Engineers TURBO EXPO99 as the best paper of the Ceramics Division. Summarized multiple years of work by the Branch’s EPM Combustor Durability Team. (Lee)
- Received the 1999 Best Paper Award from the Solar Science Division of ASME International for the paper “Thermal-Mechanical Stability of Single Crystal Oxide Refractive Concentrators for High-Temperature Solar Thermal Propulsion.” (Zhu, Jacobson, Miller)
- Paul Angel was selected by NASA Headquarters to present (11/29/99) an overview of the Special Projects Office’s funded Materials effort to Dan Goldin.
- A smoke generation system was developed for a personal-use airplane. Learjet/Bombardier’s Flight Test Center, in Witchita, KS is using the design to monitor exhaust plume flow for a study to re-direct the exhaust plume away from the vertical fin and rudder to improve controllability during maximum reverse thrust power settings. (Cuy)

Turbine Airfoil with CMC Leading Edge Concept Tested under Simulated Gas Turbine Conditions

R. C. Robinson and K. S. Hatton

Silicon-based ceramics have been proposed in gas turbine engine hot-sections. The Navy's Harrier fighter was experiencing engine (Pegasus F402) failure because of leading edge durability problems on the second stage high pressure turbine vane. The Office of Naval Research came to NASA Glenn for test support to evaluate a concept for eliminating the vane edge degradation. The High Pressure Burner Rig (HPBR) was selected for testing since it could provide the temperature, pressure, velocity and combustion gas compositions which closely simulate the engine environment. The study focused on equipping the stationary metal airfoil (Pegasus F402) with a ceramic matrix composition (CMC) leading edge insert and evaluating the feasibility and benefits of such a configuration. The test exposed the component, with and without the CMC insert, to the harsh engine environment in an unloaded condition, with cooling to provide temperature relief to the metal blade underneath.

The insert was made using an AlliedSignal Composites, Inc. enhanced HiNicalon™ fiber reinforced silicon carbide composite (SiC/SiC CMC) material fabricated via chemical vapor infiltration. The insert was 45 mils thick and occupied a recessed area in the leading edge and shroud of the vane. It was designed to be "free floating" using an end cap design. The HPBR tests provided a comparative evaluation of the temperature response and leading edge durability and included cycling the airfoils between simulated idle, lift, and cruise flight conditions. In addition, the airfoils were air-cooled, uniquely instrumented, and exposed to the exact set of both internal and external conditions, which included gas temperatures in excess of 1370 C (2500 F).

In addition to documenting the temperature response of the metal vane for comparison to the CMC, a demonstration of improved leading edge durability was a primary goal. First, the metal vane was tested for a total of 150 cycles. Both the leading edge and trailing edge of the blade exhibited fatigue cracking and "burn-through" similar to the failures experienced in service by the F402 engine. Next, an airfoil, fitted with the ceramic leading edge insert, was exposed for 200 cycles. The temperature response of those HPBR cycles indicated a reduced internal metal temperature, by as much as 600 F at the midspan location for the same surface temperature (2100 F). After testing, the composite insert appeared intact, with no signs of failure on either the vane's leading or trailing edge. Only a slight oxide scale, as would be expected, was noted on the insert.

Overall, the CMC insert performed similarly to a thick thermal barrier coating. With a small air gap between the metal and the SiC/SiC leading edge, heat transfer from the CMC to the metal alloy was low, effectively lowering the temperatures. The insert's performance has proven that an uncooled CMC can be engineered and designed to withstand the thermal up-shock experienced during the severe lift conditions which exist in the Pegasus engine. The design of the leading edge insert, which minimized thermal stresses in the SiC/SiC CMC, showed that the CMC/metal assembly can be engineered to be a functioning component.

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Thermal Conductivity Change Kinetics of Ceramic Thermal Barrier Coatings Determined by the Steady-State Laser Heat Flux Technique

D. Zhu and R. A. Miller

Ceramic thermal barrier coatings are being developed for advanced gas turbine engine components to improve engine efficiency and reliability. However, the durability of the coating systems remains a crucial issue under the conditions of increased operating temperature and extended hot exposure time that will be encountered in next generation engines. Temperature-dependent change kinetics of the coating thermal conductivity are among the most important parameters required for coating design and life prediction. Increase in thermal conductivity due to ceramic sintering can result in the reduced coating thermal insulation and increased bond coat/substrate oxidation. Therefore, determination of thermal conductivity change kinetics of thermal barrier coatings at high temperature is of great importance.

A steady-state laser heat flux technique has been developed to obtain critical thermal conductivity data of ceramic thermal barrier coatings under near-realistic temperature and thermal gradients that may be encountered in advanced engine systems [1]. The laser thermal conductivity rig consists of a 3.0 kW CO_2 continuous wave laser (wavelength 10.6 μm), a motor driven rotating test station and temperature measurement instruments such as a thermography system and infrared pyrometers. The laser surface heating and the backside air cooling determine appropriate steady-state temperature gradients across the coating systems. An integrating ZnSe lens combined with the specimen rotation can ensure a uniform laser power distribution for the specimen heating. Overall thermal conductivity changes can thus, be continuously monitored in real time, by measuring the temperature difference across the ceramic coating.

In this study, thermal conductivity change kinetics of a plasma-sprayed, 254 μm thick ZrO_2-8%Y_2O_3 ceramic coating were obtained at high temperatures. During the testing, temperature gradients across the coating system were carefully measured by the surface and back pyrometers and an embedded miniature thermocouple in the substrate. The radiation heat loss and laser absorption corrections of the ceramic coating were considered by evaluating the coating total emissivity and reflectivity. The actual heat flux passing through the coating system was determined from the metal substrate temperature drop (measured by the embedded miniature thermocouple and the back pyrometer) combined with one-dimensional heat transfer models. A significant thermal conductivity increase was observed during the laser steady-state high heat flux testing. For the ZrO_2-8%Y_2O_3 coating, the overall thermal conductivity increased from the initial value of 1.0 W/m-K to 1.15 W/m-K, 1.19 W/m-K and 1.5 W/m-K after 30 hour testing at the surface temperatures of 990°C, 1100°C, and 1320°C, respectively. The effects of heating time and temperature on the overall ceramic thermal conductivity are approximately described by a ln(k) vs. Larson-Miller relationship. The average slope of the Larson-Miller plot for the ZrO_2-Y_2O_3 coating was about 2.93×10^{-5} for the thermal barrier coating system. The increase in thermal conductivity in the TBC systems was attributed to sintering-induced micro-porosity gradients under the laser-imposed high thermal gradient conditions [1,2]. The test technique provides a viable means for obtaining coating data for use in design, development, stress modeling, and life prediction for various thermal barrier coating applications.

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Space Shuttle Wing Leading Edge Pinhole Formation

N. S. Jacobson

The space shuttle wing leading edge and nose cap are composed of a carbon/carbon composite which is protected by silicon carbide. The coefficient of thermal expansion mismatch leads to cracks in the silicon carbide. The outer coating of the silicon carbide is a sodium silicate based glass which becomes fluid at the high re-entry temperatures and fills these cracks.

Small pinholes roughly 0.1 mm in diameter have been observed on these materials after twelve or more flights. These pinholes have been investigated by researchers at Johnson Space Center, Rockwell International, Boeing, Lockheed-Martin, and Glenn Research Center to determine the possible sources and extent of damage.

These pinholes are found primarily on the wing leading edges and not the nose cap, which is covered when the orbiter is on the launch pad. The pinholes are generally associated with a bead of zinc-rich glass. Examination of the orbiter and launch structure indicates that weathering paint on the launch structure leads to zinc-containing paint flakes deposits on the wing leading edge. These may become embedded in the crevices of the wing leading edge and form the observed zinc-rich glass.

Laboratory experiments indicate that zinc oxide reacts vigorously with the glass coating on the silicon carbide. Thus, it is likely that this is the reaction which leads to pinhole formation (1). Cross sectional examination of pinholes suggests that they are enlarged thermal expansion mismatch cracks. A careful microstructural analysis indicates that walls of the pinhole consists of layers of zinc-containing glass. Thus the pinholes are likely formed by zinc oxide particles lodging in crevices and forming a corrosive zinc-rich glass. This corrosive glass enlarges existing cracks and leads to pinholes (2).

Having established the likely source of the pinholes, the next step was to model the damage (3). The concern is that if a pinhole goes through the silicon carbide to the carbon/carbon substrate, oxygen would have a clear path to oxidize the carbon at high temperatures. This possibility was examined with studies in a laboratory furnace. An ultrasonic drill was used to make artificial pinholes in a sample of protected carbon/carbon. After exposure the specimens were weighed and cross-sectioned to quantify the extent of oxidation below the pinhole.

The results at higher temperatures showed good agreement with a simple diffusion-control model. This model is based on the two-step oxidation of carbon to carbon monoxide and carbon dioxide. The model indicates a strong dependence on pinhole diameter. For smaller diameters and short times, the oxidation of carbon is very limited.

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Diagnostics in Chemical-Vapor-Deposited Diamond Films

K. Miyoshi

The advantages and utility of chemical-vapor-deposited (CVD) diamond as an industrial ceramic can only be realized if the price and quality are right. Until recently, this technology was of interest only to the academic and basic research community. However, interest has grown because of advantages made by leading CVD diamond suppliers (ref. 1):

1. Reduction of the cost of CVD polycrystalline diamond deposition below \$5/carat (\$8/cm^2)
2. Installation of production capacity
3. Epitaxial growth of CVD single-crystal diamond achieved

Thus, CVD diamond applications and business are an industrial reality. At present CVD diamond is produced in the form of coatings or wafers. CVD diamond film technology offers a broader technological potential than do natural and high-pressure synthetic diamonds because size, geometry, and eventually cost will not be as limiting. Now that they are cost effective, diamond coatings —with their extreme properties—can be used in a variety of applications. Diamond coatings can improve many of the surface properties of engineering substrate materials, including erosion-, corrosion-, and wear-resistance. Examples of actual and potential applications, from micro-electro-mechanical systems (MEMS) to wear parts, of diamond coatings and related superhard coatings are described in reference 2. For example, diamond coatings can be used as a chemical and mechanical barrier for Space Shuttle's check valves, particularly guide pins and seat assemblies (ref. 3).

To achieve satisfactory surface and bulk properties of coatings and films, it is necessary to optimize deposition parameters through study of the physical, chemical, and structural changes of coatings and films as a function of deposition parameters (ref. 4). These parameters must not only give the appropriate initial level of surface and bulk properties, but must also provide durable coatings and films.

For a material to be recognized as diamond it must have all of the following characteristics (refs. 1 and 4):

1. Crystalline diamond morphology and microstructure visible by electron microscopy
2. Single-phase diamond crystalline structure detectable by x-ray or electron diffraction
3. Clear, sharp diamond peak at 1332 cm^{-1} in a Raman spectrum
4. Contains carbon
5. Low equilibrium coefficient of friction (0.01 to 0.05) in air

Diagnostic techniques, including friction measurement, have been highlighted in an important case study of microwave-plasma-assisted CVD diamond films (ref. 4). The work focused attention primarily on the nature, character, and quality of the CVD diamond films. Diagnostic techniques include:

1. Scanning electron microscopy and transmission electron microscopy (SEM and TEM), to determine surface morphology, microstructure, and grain size
2. Surface profilometry and atomic force microscopy (AFM), to measure surface roughness and to determine surface morphology
3. Rutherford backscattering (RBS) and elastic recoil spectroscopy (ERS), to determine the composition (including hydrogen)
4. Raman spectroscopy, to characterize the atomic bonding state and quality of diamond
5. X-ray diffraction (XRD), to determine the crystal orientation of diamond
6. Friction examination, to determine the coefficient of friction and surface properties

The commercial potential of diamond films has been clearly established and a number of applications have been identified through university, industry, and government research studies. A combination of diagnostics techniques can provide the technical information required to understand the characteristics and properties of diamond films which are important to their application in specific component systems and environments (refs. 1, 4, and 5).

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Near Net Shape Processing of Sintered Fibrous Ceramics

P. W. Angel

A variety of sintered fiber ceramic (SFC) materials have been developed over the last fifty years as thermal barrier materials for re-entry applications. SFC typically exhibit very low thermal conductivities combined with low density and good thermal stability up to 2500°F. These materials have flown successfully on the Space Shuttle orbiters since the 1960's. More recently, the McDonnell Douglas DC-X vehicle successfully used SFC tiles as a heat shield on the underside of the test vehicle. For both of these applications, tiles are machined from blocks of a specific type of SFC called alumina enhanced thermal barrier (AETB). The sizes of the blocks are limited due to the manufacturing process. In addition, as much as 80-90% of the material can be lost during the machining of tiles with significant amounts of curvature. Under a contract with Boeing and in cooperation with NASA Glenn Research Center, a vacuum-assisted forming process has been developed that can produce large (approximate four foot square), severely contoured shaped panels of AETB while providing cost savings over the conventional cast-and-machine billet process.

For Shuttle use, AETB is slurry cast, drained and fired to form square billets conforming to the shape of the filtration box. The billets are then cut into tiles of appropriate size to be used for thermal protection of the Space Shuttle. Current processing techniques limits the maximum size of AETB billets to 21.5 inches square and 6.5 inches thick. The Space Shuttle uses discrete heat shield tiles no more than 8-12 inches square. In other applications, large complex shapes are needed and the tiling approach is undesirable. For such applications, vacuum-assisted forming can produce large, complex shaped parts while reducing machining waste and eliminating cemented joints between bonded billets. Because it allows the forming of contoured shapes, material utilization is inherently high. Initial estimates show that the amount of material lost during machining can be reduced by as much as 50%, or more. In addition, a fiber alignment favorable for minimum heat transfer is maintained for all panel shapes since the fibers are aligned parallel to the contoured surface of the forming tool or mold. The vacuum-assisted forming process is capable of completing the entire forming operation in a matter of minutes and can produce multiple parts whose size is limited only by the size of the forming tool. Panels as large as two feet square have been demonstrated to-date.

The vacuum-assisted forming process starts with the fabrication of a permeable forming tool, or mold, with the proper part contour. This reusable tool is mounted over an internal rib support structure, such that a vacuum can be pulled on the bottom portion of the tool. AETB slurry is then poured over and around the tool and the part is formed as the liquid is drawn from the slurry and the part forms over the tool surface. The part is then dried, fired and finished machined. Future plans include an evaluation of the need for additional coatings and surface-toughness treatments to extend the durability and performance of this material.

Analytical Science Group FY’99 Highlights

Over 4747 Samples Analyzed in FY'99 (FY’98 4300)

CHEM	X-RAY	METLAB	SEM	PROBE	TEM
803 (725)	880 (1047)	1583 (1907)	849 (371)	28 (99)	570 (157)

Initiation of database for tracking ASG requests/financial data. (Auping/O’Donnell)

Developed dissolution methods for W-based materials, containing Hf, Zr, and Y, for ICP analysis. (Nawalaniec/Kiser)

Provided corrosion data relating to the KC-135 Microgravity Experiment. (Nawalaniec/Fritz).

Composition, impurity, and oxygen analysis of Cu-Cr-Nb for RLV applications. (Johnson/Nawalaniec/Ellis)

Metallographic preparation of Au coated Mo to verify new traveling wave tube manufacturing techniques. (McQuater/Petko/Kory)

Microprobe analysis of TiAl oxide scales after 7000 hour exposure. (Smith/Locci)

Examination of GE PtAl/carburizing treatment to understand beneficial effects of carburizing. (Garg/MacKay/Ritzert)

TEM study of gamma' size-distribution/morphology of advanced turbine disk. (Garg/Ellis/Gabb)

Tripod polishing of ceramic composites provides superior samples (Chen/Bansal/Bhatt/Yun)

Gatan Image Filter used to identify <10 nm carbon layer in SiC/SiC composite (Chen/Yun)

SEM/TEM of carbon nanotubes produced by combustion synthesis. (Chen/Hull/McCue/VanderWal)

New Equipment; XRF software upgrade Microwave dissolution system

JEOL 840A Motorized Stage Upgrade

Struers' Electropolisher

Microprobe XEDS Upgrade